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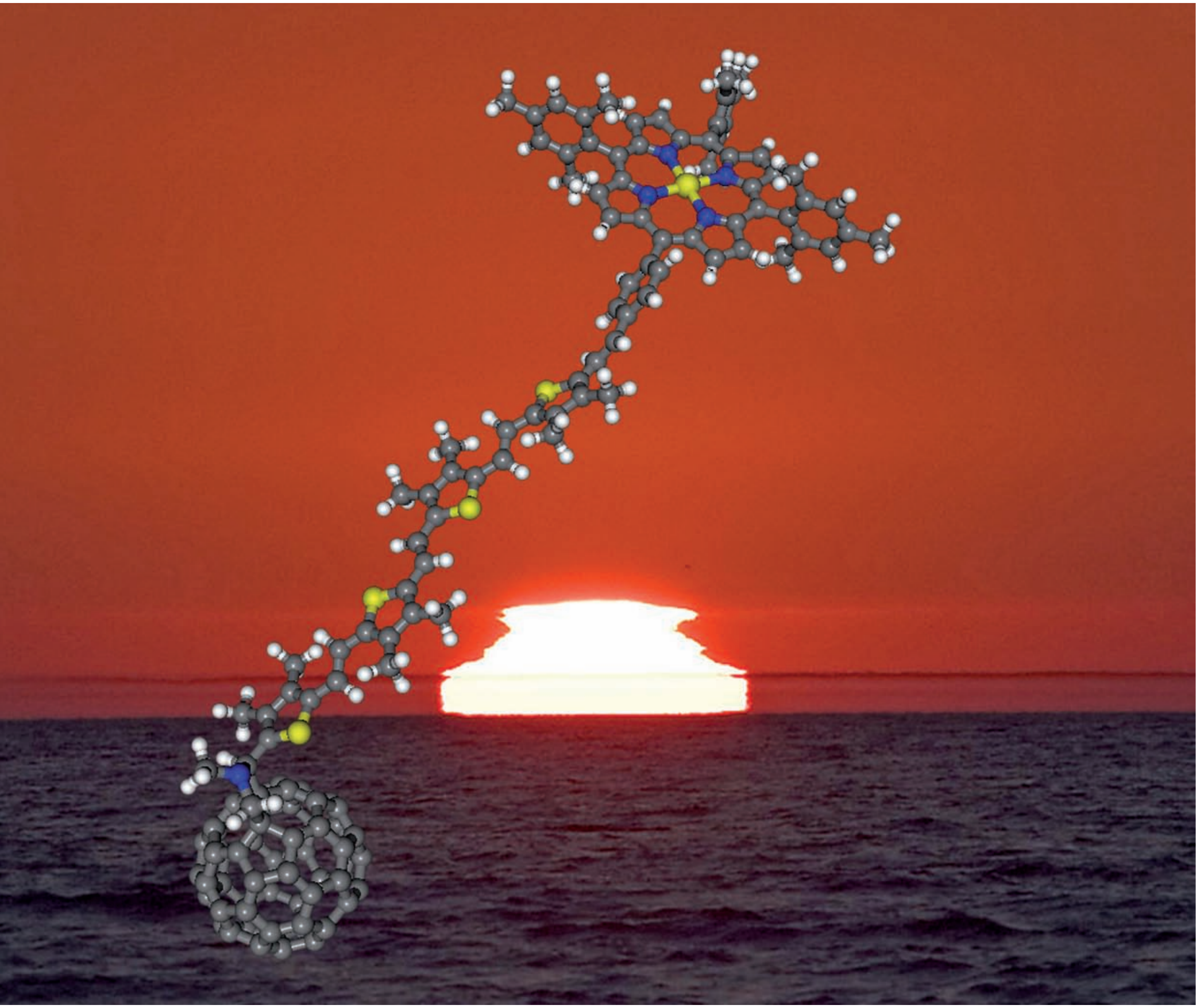

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Osamu Ito, Fernando Langa *et al.*

High effectiveness of oligothienylenevinylene as molecular wires in Zn-porphyrin and C_{60} connected systems

High effectiveness of oligothienylenevinylene as molecular wires in Zn-porphyrin and C_{60} connected systems†

Frédéric Oswald,[a] D.-M. Shafiqul Islam,[bc] Yasuyuki Araki,[b] Vincent Troiani,[a] Ruben Caballero,[a] Pilar de la Cruz,[a] Osamu Ito*[b] and Fernando Langa*[a]

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Photoinduced energy transfer and electron transfer processes have been found between the excited singlet state of Zn-porphyrin and C_{60} *via* an oligothienylenevinylene bridge depending on the length of the oligothiophene and solvent polarity.

One-dimensional nanostructures such as nanowires have become the focus of intensive researches due to their potential uses in devices including sensors, electronics and optoelectronics. Linear π-conjugated oligomers with well-defined chemical structures have been used as molecular wires in molecular electronics or nanoscopic systems;[1] moreover, photoinduced electron transfer in donor–bridge–acceptor systems, where the bridge is a π-conjugated oligomer, exhibits weak distance dependence for donor–acceptor distances as long as 40 Å.[2] Among the different π-conjugated oligomers, oligothienylenevinylene oligomers (*n*TVs) have been described as excellent wires,[3] similar to other conjugated oligomers.[4]

Molecular architectures formed by porphyrins and fullerenes linked by various bridging groups have been the subject of numerous studies in recent years.[5] For example, oligothiophene (OT)[6] and oligophenylenevinylene (OPV) moieties[7] have been shown to act as long distance molecular wires in the efficient photoinduced electron transfer from the porphyrin chromophore to the fullerene. Although C_{60}–*n*TV dyads have been investigated in which *n*TVs act as electron donors,[8] triads in which *n*TVs act as wires between porphyrins and fullerene have not been reported to date despite the potential interest in such systems.

We report here the synthesis of novel ZnP–*n*TV–C_{60} donor–acceptor systems that incorporate a Zn-porphyrin (ZnP) as the donor and fullerene (C_{60}) as the acceptor, with these units bridged by *n*TV units. In addition, the dependence of the photoinduced energy-transfer and electron-transfer processes on solvent polarity was investigated. Charge-separation quantum yields close to unity and lifetimes of the charge-separated state as long as one microsecond were found for the ZnP–*n*TV–C_{60} triad **4b** (Chart 1).

In the first step, ZnP–*n*TV systems **3a,b** were synthesized by Wadsworth–Emmons olefination between phosphonateporphyrin **1**[9] and bisformyl-oligomers **2a,b**,[10] bearing alkyl groups to afford solubility, under careful stoichiometric control to give yields of 42 and 54%, respectively. Compound **1** was prepared according to the Lindsey method.[8] The target molecules **4a,b** were prepared by 1,3-dipolar cycloaddition between **3a,b**, *N*-methyl glycine and C_{60} in chlorobenzene in good yield (49% in both cases) (see ESI† for details on the characterization, Fig. S1–S6). Optimized structures and the HOMO and LUMO of **4a,b** were evaluated by Gaussian calculations (ESI;† Fig. S7), which suggest that the charge-separated states are $ZnP^{\bullet+}$–*n*TV–$C_{60}{}^{\bullet-}$.

The redox potentials, detected by OSWV (*vs.* $Ag/AgNO_3$ in *o*-DCB–acetonitrile (4 : 1) solution (0.1 mol dm^{-3} Bu_4NClO_4) at room temperature), of ZnP–2TV–C_{60} (**4a**) showed a one-electron reduction potential of the C_{60} moiety at −1.07 V whereas the oxidation potential appeared at 0.35 V. These findings can be attributed to the overlapped peaks of both ZnP and 2TV, a situation consistent with the possibility of $ZnP^{\bullet+}$–2TV–$C_{60}{}^{\bullet-}$ and ZnP–$2TV^{\bullet+}$–$C_{60}{}^{\bullet-}$ being present in an equilibrium. In the case of ZnP–4TV–C_{60} (**4b**), one-electron oxidation potentials at 0.16 and 0.29 V *vs* $Ag/AgNO_3$ were observed. These values can be attributed to 4TV

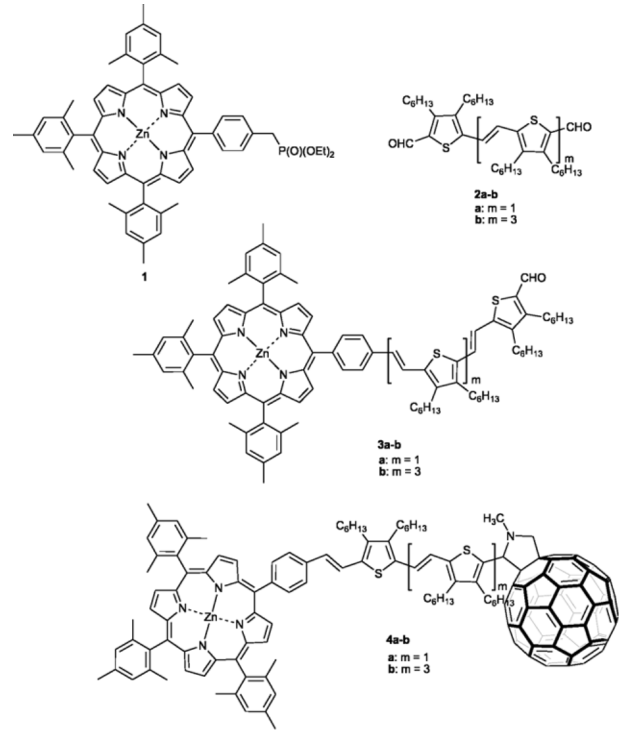

Chart 1 Triads **4a,b** and the corresponding starting compounds (**1**, **2a,b**, **3a,b**).

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[a] *Facultad de Ciencias del Medio Ambiente, Universidad de Castilla-La Mancha, 45071, Toledo, Spain*
[b] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira Sendai, 980-8577, Japan*
[c] *Department of Chemistry, Jahangirnagar University, Savar, Dhaka, Bangladesh*

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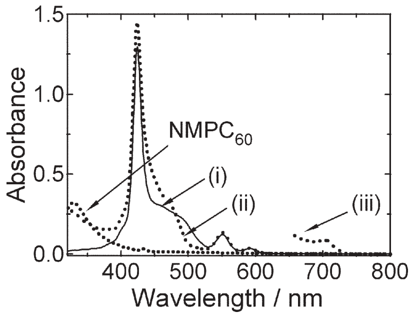

Fig. 1 Absorption spectra in toluene: (i) ZnP–2TV (**5a**), (ii) **4a** (ZnP–2TV–C_{60}), (iii) magnified spectrum (×50) of C_{60} absorption of **4a** and NMP–C_{60} (*N*-methylfulleropyrrolidine).

and ZnP, respectively, and provide evidence that ZnP–$4TV^{•+}$–$C_{60}^{•-}$ is more stable than $ZnP^{•+}$–4TV–$C_{60}^{•-}$.

The electronic absorption spectrum of **4a** in toluene (Fig. 1) can be understood as a simple superposition of the electronic transitions of the three constituent chromophores: *i.e.*, the Zn-porphyrin (**1**) displays a very strong absorption band at 422 nm (Soret band) and the π–π* transition of the 2TV appears as a shoulder on the strong Soret band between 450 and 500 nm. The absorption peaks at 320 and 700 nm can be attributed to the C_{60} moiety. The sum of the absorption intensities for ZnP–2TV and NMP–C_{60} (*N*-methylfulleropyrrolidine) is slightly lower than that for ZnP–2TV–C_{60} at 330 and 500 nm, which can be attributed to the shifts of the bands due to weak interaction among the chromospheres in the ground state. In the case of **4b**, the 4TV absorption appeared to 500–600 nm and superimposed over the Q bands (ESI;† Fig. S8), while other absorption peaks are similar to those of **4a**.

The emission spectra of the triad **4a** are shown in Fig. 2 along with those of the reference compounds ZnP–2TV (**5a**). The fluorescence spectra of **4a** in toluene (Fig. 2(a)) and in benzonitrile (PhCN) (Fig. 2(b)) upon irradiation of the Soret band (λ_{ex} = 420 nm) of the ZnP moiety are also shown. In **4a** the fluorescence intensity of the $^1ZnP^*$ moiety (maxima at 600 and 650 nm in toluene) was markedly reduced (by a factor of at least 98%) compared with ZnP–2TV by the fullerene attached on the opposite side of 2TV. In toluene, the appearance of a peak at 715 nm, due to the fluorescence of the fullerene, indicates energy transfer (EnT) from the $^1ZnP^*$ moiety to the C_{60} moiety either directly or indirectly.[11] In PhCN the decrease in the fluorescence was observed without the appearance of $^1C_{60}^*$-fluorescence; thus, the fluorescence quenching can be attributed to the charge-separation generated by $ZnP^{•+}$–2TV–$C_{60}^{•-}$ as the first step, a process that has a negative ΔG_{CS} value in PhCN.

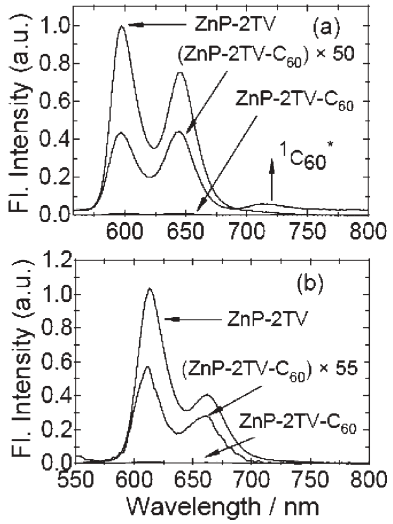

Fig. 2 Steady-state fluorescence spectra of **4a** (ZnP–2TV–C_{60}) and **5a** (ZnP–2TV) in (a) toluene and (b) PhCN, λ_{ex} = 420 nm.

The EnT and charge-separation processes in **4a** (ZnP–2TV–C_{60}) in toluene were further confirmed by the time-resolved fluorescence spectra (ESI;† Fig. S9), in which the persistent $^1C_{60}^*$-fluorescence was confirmed in the 700–800 nm region after the decay of $^1ZnP^*$-fluorescence;[11] however, such persistent $^1C_{60}^*$-fluorescence was not observed in PhCN. In the case of **4b** (ZnP–4TV–C_{60}), the fluorescence intensities of the $^1ZnP^*$ moiety decreased in toluene and PhCN without the appearance of $^1C_{60}^*$-fluorescence, suggesting predominant charge-separation *via* $^1ZnP^*$ in both solvents.

The $^1ZnP^*$-fluorescence lifetimes of ZnP–2TV–C_{60} (**4a**) were evaluated to be 53 ps in toluene and 86 ps in PhCN from the $^1ZnP^*$-fluorescence decay time profiles (ESI;† Fig. S10). The rate constant for the EnT (k_{EnT}) in toluene was evaluated to be 1.8×10^{10} s^{-1}. In PhCN the rate constant of $^1ZnP^*$-fluorescence quenching (k_q) can be calculated to be 1.2×10^{10} s^{-1}, which mainly includes the charge-separation rate constant (k_{CS}). For ZnP–4TV–C_{60} (**4b**) the $^1ZnP^*$-fluorescence lifetimes have two components, which give short initial lifetimes [138 ps (65%) in toluene and 107 ps (64%) in PhCN] and longer lifetimes (1065 ps in toluene and 971 ps in PhCN), which can be attributed to different conformations such as fully extend structure.[12] The k_{CS} values were evaluated on average to be 6.7×10^9 and 8.8×10^9 s^{-1} in toluene and PhCN, respectively. The k_{CS} values in PhCN decrease with *n*TV and this gives a small damping factor for the charge-separation constants (k_{CS}), which shows the effectiveness of *n*TV as a molecular wire.

In an effort to obtain direct evidence for the energy transfer and charge-separation processes, the transient absorption spectra were measured. In toluene, the band at 760 nm (with a shoulder at 800 nm) was observed along with the band at 600 nm for **4a** in toluene after the 355-nm nanosecond laser light pulse excitation (ESI;† Fig. S11). These bands are attributed to the triplet states of 2TV (^{3}2TV*), ZnP ($^3ZnP^*$) and C_{60} ($^3C_{60}^*$). This fact is consistent with the EnT processes occurring from $^1ZnP^*$ to C_{60}, producing $^1C_{60}^*$, followed by the generation of $^3C_{60}^*$ *via* an intersystem crossing process.

In PhCN (Fig. 3) an additional transient absorption peak was observed at 1020 nm and this is the diagnostic peak for $C_{60}^{•-}$. The shoulder at 620 nm observed at 1000 ns was assigned to $ZnP^{•+}$, suggesting the generation of $ZnP^{•+}$–2TV–$C_{60}^{•-}$. On the other hand, the 720 nm band with a shoulder at 800 nm can be attributed to $2TV^{•+}$, suggesting the co-existence of ZnP–$2TV^{•+}$–$C_{60}^{•-}$. The decay of $C_{60}^{•-}$ can be fitted with a mono-exponential function, giving a charge-recombination rate (k_{CR}) of 1.8×10^6 s^{-1}, which corresponds to the lifetime of the charge-separated state as 550 ns.

Absorption bands appeared at 700, 760 and 1020 nm for **4b** (ZnP–4TV–C_{60}) in toluene and PhCN (ESI;† Fig. S12) upon excitation with 355-nm laser light, indicating that the ZnP moiety and 4TV moiety are excited along with a small amount of the C_{60} moiety. The 1020 nm band can be attributed to $C_{60}^{•-}$. The intense absorption band at 760 nm is mainly attributed to the triplet state

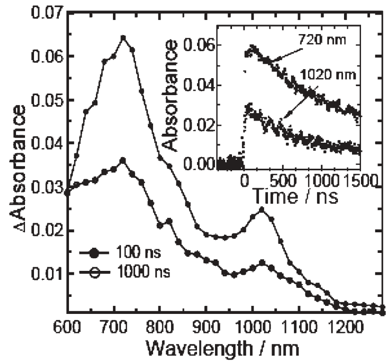

Fig. 3 Transient absorption spectra of **4a** (0.1 mM) in Ar-saturated PhCN obtained by 355-nm laser light irradiation. Inset: Absorption time profiles.

of 4TV (^{3}4TV*) and the absorption bands of ^{3}ZnP* and ^{3}C$_{60}$* may be overlapped with this. The absorption bands of 4TV$^{\bullet+}$ are expected to appear at 660, 950 and 1120 nm[13] but they were very weak in the observed transient absorption spectrum at 100 ns. This indicates that ZnP–4TV$^{\bullet+}$–C$_{60}$$^{\bullet-}$ generation is minor; this species is generated either by hole-shift (HS) from an initial charge-separated state such as ZnP$^{\bullet+}$–4TV–C$_{60}$$^{\bullet-}$ *via* ^{1}ZnP* or by charge-separation directly *via* ^{1}C$_{60}$*. This HS process in ZnP$^{\bullet+}$–4TV–C$_{60}$$^{\bullet-}$ may be competitive with the charge-recombination process, generating the triplet states of ZnP* and ^{3}C$_{60}$*. The k_{CR} value was evaluated to be 0.6×10^6 s^{-1} from the decay at the 1020-nm band. Thus, the lifetime of the charge-separated state was evaluated to be 1670 ns in toluene.

In PhCN, the combination of the 1020 nm band with the 660, 860 and 1200 nm bands shows the presence of ZnP–4TV$^{\bullet+}$–C$_{60}$$^{\bullet-}$ even after 100 ns. This species could be generated from the initial charge-separated state (ZnP$^{\bullet+}$–4TV–C$_{60}$$^{\bullet-}$) *via* HS. A k_{CR} value of 0.5×10^5 s^{-1} was evaluated on the basis of the time profile at 1020 nm in PhCN (ESI;† Fig. S12b) and, from this constant, the lifetime for ZnP–4TV$^{\bullet+}$–C$_{60}$$^{\bullet-}$ was evaluated as 2000 ns. The k_{CR} value in PhCN was also slightly lower than that in toluene. Compared with the k_{CR} value for ZnP–2TV$^{\bullet+}$–C$_{60}$$^{\bullet-}$ in equilibrium with ZnP$^{\bullet+}$–2TV–C$_{60}$$^{\bullet-}$ in PhCN, the k_{CR} value of ZnP$^{\bullet+}$–4TV–C$_{60}$$^{\bullet-}$ is markedly smaller (by a factor of 1/3), although the charge-recombination processes are different. The ratios of k_{CS}/k_{CR} were evaluated to be *ca.* 10^5, indicating that **4a,b** (ZnP–*n*TV–C$_{60}$) are efficient charge-separation systems that stabilize the charge-separated states.

In summary, an energy diagram can be depicted as shown in Fig. 4. Since the four chromophores ZnP, C$_{60}$, 2TV and 4TV have their triplet states, which are generated through intersystem crossing from the excited singlet states and charge-recombination of the charge-separated states higher in energy than these triplet states,[11] the transient spectra became complicated due to overlap with the absorption bands of radical ions such as ZnP$^{\bullet+}$, C$_{60}$$^{\bullet-}$, 2TV$^{\bullet+}$ and 4TV$^{\bullet+}$. The processes that occur *via* ^{1}ZnP* are clearly revealed on combination of the fluorescence data and transient absorption data. For short *n*TV units in a nonpolar solvent, energy transfer takes priority over charge separation, whereas in PhCN the charge-separation predominantly occurs because of the stabilization of the charge-separated state. In the case of longer *n*TV units in a nonpolar solvent, the charge-separation prevails over energy transfer. The small damping factor for the charge-separation *via* ^{1}ZnP* in PhCN suggests the effectiveness of *n*TV as molecular wire. We are currently extending the *n*TV unit in ZnP–*n*TV–C$_{60}$.

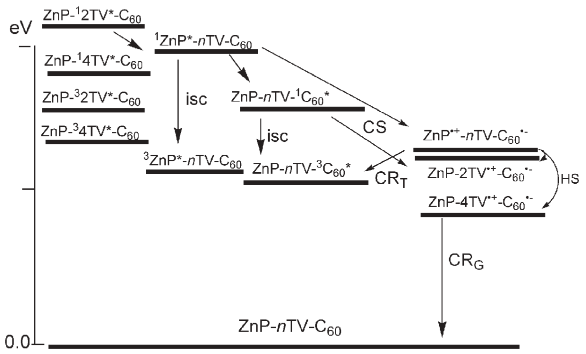

Fig. 4 Energy diagram and proposed photophysical processes.

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